

# MICROSTRUCTURAL INVESTIGATION OF CALCINED AND SULFATED LIMESTONE FOR THE UTILIZATION IN THE AFBC ENVIRONMENT

Hyung-Taek Kim, Dong-Hyung Kim\*, Hong-Tae Kim\*\*,  
and Hyukbo Kwon\*\*\*

Department of Energy, Ajou University 5, Woncheon-Dong, Suwon, Korea 441-749

\*Dept. of Solar Thermal Energy, Korea Institute of Energy Research

\*\*Dept. of Civil Engineering, Kyungbuk National University

\*\*\*Dept. of Environmental Protection, Kyungnam University

## ABSTRACT

Major parameters determining the extent of Ca utilization were investigated for their calcination/sulfation behavior of limestone in the AFBC(Atmospheric Fluidized Bed Combustion) environments. Three different particle sizes of Fredonia limestone were investigated in the lab-scale tubular reactor. The results of the calcination conversion of limestone imply that the decomposition rate of  $\text{CaCO}_3$  into CaO is dependent on the amount of heat which limestone absorbed. Hg porosimeter measurement of calcined limestone illustrated that surface area and pore volume are increased with decreasing particle size. Raw Fredonia limestone and sequentially as well as simultaneously calcined/sulfated limestones were also examined using SEM. The SEM Studies showed that the surface of the calcined limestone particles is more diffusive nature than that of the parent calcite. However, the sulfur distribution pattern of simultaneously-treated particles and that of the sequentially-treated one shows no difference.

## 1. INTRODUCTION

The amount of coal used as a source of energy in utility application is expected to increase in spite of pressing economic and environmental factors. In part, the viewpoint is a result of the emergence of technologies, like atmospheric fluidized bed combustion(AFBC), that offer dramatic possibilities for the combus-

tion of coal in an environmentally acceptable manner. In AFBC, coal is introduced into a fluidized bed with noncombustible solid of limestone. During the combustion of coal, sulfur content in coal is oxidized to sulfur oxides. The limestone acts as a sulfur sorbent material which is removed from the bed as a dry, solid waste. In the typical temperature range of AFBC (800~850°C), calcite ( $\text{CaCO}_3$ ) in limes-

tone is calcined to calcia (CaO). The CaO reacts with the SO<sub>2</sub> that is released during coal combustion and forms anhydrite (CaSO<sub>4</sub>), a solid reaction product.

Differences in the extent of Ca utilization depend on characteristics of the limestone such as porosity, microstructure, and the size of the stone, in addition to its residence time in the combustor and the processing conditions to which the stone is exposed. The molar volume of CaSO<sub>4</sub> is 45.9cc/g-mole<sup>1)</sup> which is greater than the molar volume of either CaCO<sub>3</sub> or CaO. Hence, if particle shrinkage/expansion is neglected during CaSO<sub>4</sub> formation, all of the pore volume created during calcination would be filled before all of the CaO could be sulfated. On such a basis of molar volume differences, the maximum amount of CaO that could be sulfated is 69%. Thus, in order to attain sulfation conversion greater than 69%, limestone must have either some initial pore volume or excess pore volume must be created during calcination. In reality, all of the pore volume within CaO may not be available during the sulfation reaction. For example, pores below a limiting size plug quickly and will not be available to the sulfation process.

It has also been generally observed that entire limestone particles develop exterior sulfation shells which eventually terminate the sulfation reaction. Such a sulfation shell has been modeled by Szekeley and Evans<sup>2)</sup> to illustrate near surface grain and grain boundary sulfation as a function of time<sup>3)</sup>. The application of this grain boundary theory to sulfur sorption by limestone has resulted in some reasonable agreement with experimental data in the 800~950°C temperature range<sup>4)</sup>. This grain model predicts the formation of a dense outer shell of CaSO<sub>4</sub> on a CaO core after 15 minutes of SO<sub>2</sub> exposure; consequently, the sulfation process will effectively terminate in any limestone particle that contains a CaSO<sub>4</sub> shell.

In the present experiment, the research has focused on the microstructural characterization of sized fractions of Fredonia limestone in its calcined, sulfated, and simultaneously calcined/sulfated forms to determine the sulfur capture behavior of limestone in the AFBC condition.

## 2. EXPERIMENTAL

Limestone used in the present experiment is obtained from the quarry in Fredonia region of western Kentucky, USA. It contains about 98% CaCO<sub>3</sub>. Fredonia limestone samples were crushed and classified into three different size fractions. Each size fraction of limestones was subjected to investigate in the AFBC-simulated tubular reactor. The schematic of the experimental system including tubular reactor is shown in Fig. 1<sup>5)</sup>. Pre-weighed limestone particles are wrapped with ceramic cloth to prevent particle loss due to popping behavior at the high temperature. The limestone was rapidly injected into the reactor to simulate shock treatment and subsequently extracted from the reactor under a dry N<sub>2</sub> cooling condition. After predetermined time period, samples were withdrawn from the reactor and weight change of the samples was measured. From the weight measurement, the conversion efficiencies of calcination and sulfation were calculated<sup>6)</sup>.

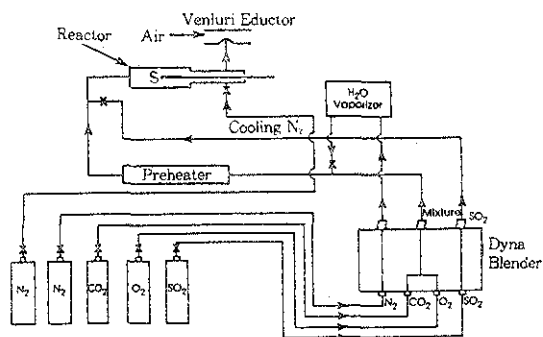


Fig. 1. Schematic of Experimental System.

For the entire investigation, Fredonia limestone was subjected to investigate in the calcining and sulfating environments that are similar to those encountered in atmospheric fluidized bed combustion. These environments were generated in a reactor through which gases containing  $O_2$ ,  $CO_2$ ,  $H_2O$ ,  $N_2$  and  $SO_2$  were flowed. Preselected compositions ( $CO_2=15\%$ ,  $O_2=5\%$ ,  $H_2O=8\%$ ,  $SO_2=0.5\%$  and  $N_2=balance$ ) are preheated to specified temperatures ( $800\sim 850^\circ C$ ) before admission to the reactor. The  $SO_2$  is admitted to the  $O_2-CO_2-H_2O-N_2$  gas mixture after passing through the preheater but before the reactor. This configuration enables calcination/sulfation experiments to be performed separately or simultaneously.

Calcined limestones were examined by Hg porosimeter (Quantachrome) to provide informations of surface area and pore volume. Raw Fredonia limestone and sequentially and simultaneously calcined/sulfated limestones were also examined using SEM and EDX to provide microstructural and compositional information of calcined/sulfated limestone. Subjected particles were mounted into the epoxy resin. Fresh surface of the samples was exposed by using diamond cut followed by surface grinding/polishing.

### 3. RESULTS AND DISCUSSION

The conversion time for Fredonia limestone to CaO was determined after exposure to gas compositions of 15%  $CO_2$ , 5%  $O_2$ , 8%  $H_2O$  and 72%  $N_2$  at  $850^\circ C$ . Fig. 2 showed that complete conversion time to calcination was increased with particle size. The critical time for complete calcination are 15 minutes for  $0.2\sim 0.6mm$ -diameter limestone, 20 minutes for  $1.0\sim 1.7mm$ -diameter limestone, and 25 minutes for  $2.0\sim 2.4mm$ -diameter limestone. The percent conversion to CaO for  $1.0\sim 1.7mm$ -diameter Fredonia limestone as a function of time and temperature is

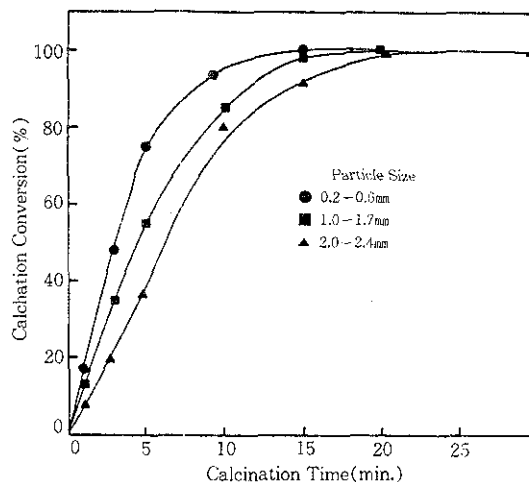


Fig. 2. Calcination Conversion Versus Time for Different Particle Size Limestone.

also shown in Fig. 3. The results on the calcination conversion of limestone imply that the decomposition rate of  $CaCO_3$  into CaO is dependent of the amount of heat absorbed.

To verify aforementioned calcination behavior of Fredonia limestone, calcined samples were analyzed by mercury porosimeter to check pore volume and surface area with respect to weight loss. These results, shown in Fig. 4, complement the weight analysis data. In addition, the smallest limestone particles contain the

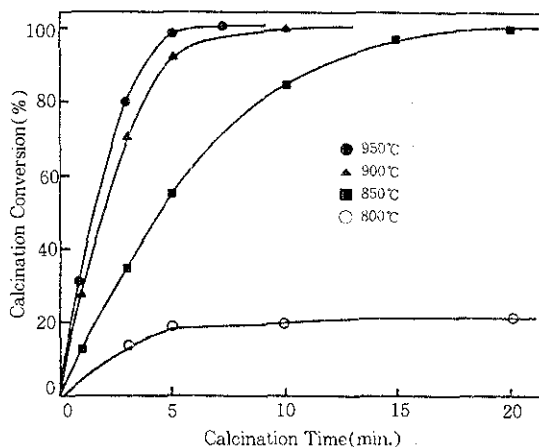


Fig. 3. Calcination Conversion of Fredonia Limestone Versus Time for Different Temperatures.

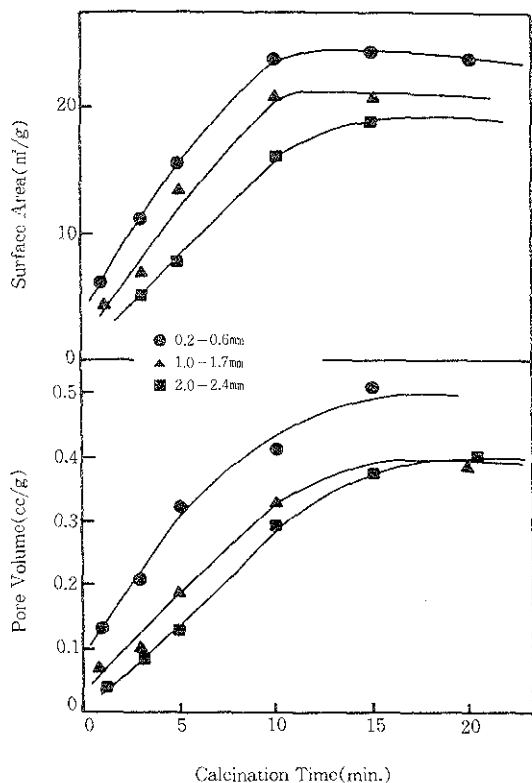


Fig. 4. Pore Volume and Surface Area Change During Calcination in the Typical AFBC Exhaust Gas Environment.

largest surface area and total pore volume. Interestingly, the surface area of limestone is constant after certain period whereas the pore volume continues to increase for small- and medium-sized samples. The pore volume distribution after different calcination time is plotted against pore diameter in Fig. 5 for medium-sized limestone. A longer calcination time results in an increase of the average size of the pores. This kind of behavior was also found for the large and small limestone particles

Fig. 6 shows the SEM micrographs of a cross-sectioned particle of Fredonia limestone which illustrated the heterogeneous nature. The particle consists of at least three phases of  $\text{CaCO}_3$ , including elongated structures (fossil remnants), circular or near-circular structures

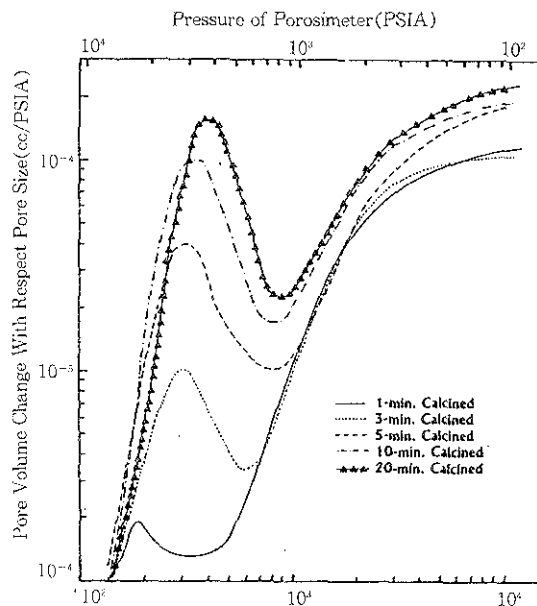


Fig. 5. Change of Pore Volume Distribution During Calcination of Fredonia Limestone.

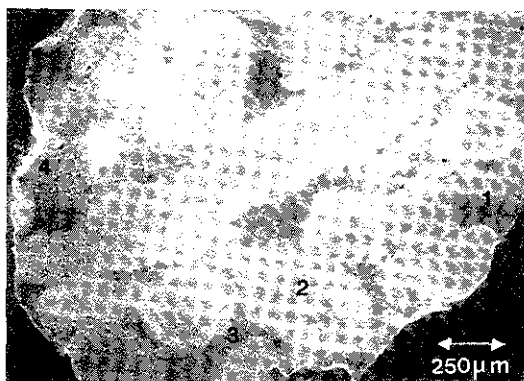


Fig. 6. SEM micrograph of Raw Fredonia Limestone. (A Single, Cross-sectioned Particle).

(fossil remnants or oolitic limestone), and relatively large-grained, smooth portions. At higher magnifications, the morphological and structural differences of the limestone can be more easily discerned. Fig. 7, an magnified SEM micrograph of position I in Fig. 6, shows an interface region between finely divided, porous  $\text{CaCO}_3$  and larger grained  $\text{CaCO}_3$  (about 25

microns). Fig. 8, obtained from point 2 in Fig. 6, depicts the highly porous and central region of a fossil remnant. The SEM micrograph in Fig. 9 and 10 obtained from points 3 and 4 in Fig. 6, respectively, shows that the area of the particle between fossil remnants and oolites is non-porous and of large grain size (30~180 microns in diameter) in addition to porous and of small grain size (about 20 microns). The heterogeneity of Fredonia limestone can of course, be explained relative to its geological formation<sup>7)</sup>. With respect to the formation of cracks on the particle surface during calcination, the features shown at the edge of the

cross-sectioned particle in Fig. 10 and at the boundary between large-grained  $\text{CaCO}_3$  and small-grained  $\text{CaCO}_3$  would contain structural release lines which could accommodate cracking.

Fig. 11 are SEM micrographs of Fredonia limestone after calcination at 850°C for 20 minutes followed by sulfation at 850°C for 20 minutes. The S map in Fig. 12 shows that S has penetrated into some regions within the central portion of limestone particles whereas other areas of these particles, including near-edge locations, do not contain S. The microstructure of various areas of Fig. 11 provide



Fig. 7. SEM micrograph of Raw Fredonia Limestone. (Position 1 in Fig. 6.)

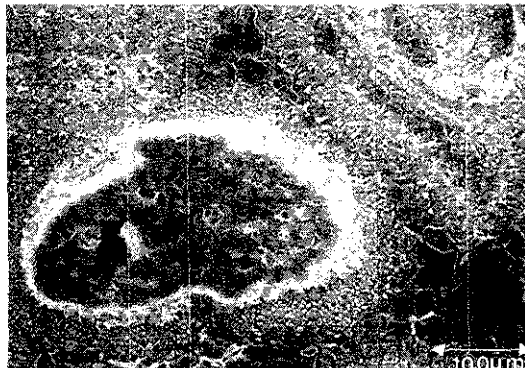


Fig. 9. SEM micrograph of Raw Fredonia Limestone. (Position 3 in Fig. 6.)

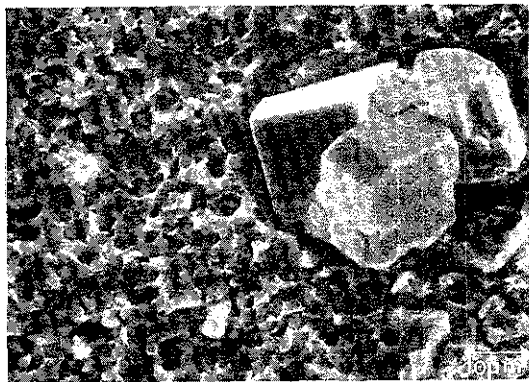


Fig. 8. SEM micrograph of Raw Fredonia Limestone. (Position 2 in Fig. 6.)

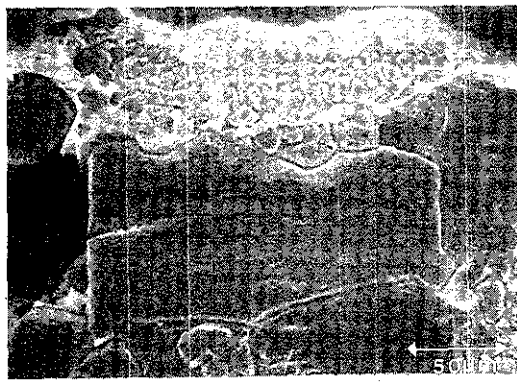


Fig. 10. SEM micrograph of Raw Fredonia Limestone. (Position 4 in Fig. 6.)

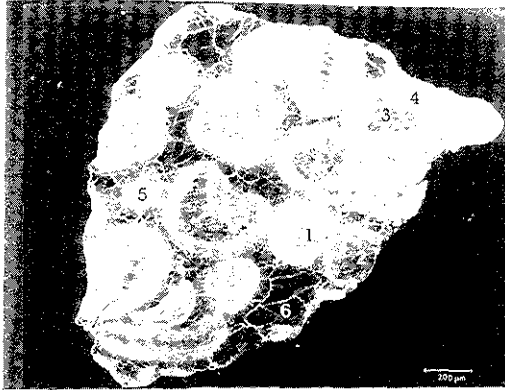


Fig. 11. SEM micrograph of Sulfated Fredonia Limestone. (A Single Cross-sectioned Particle)

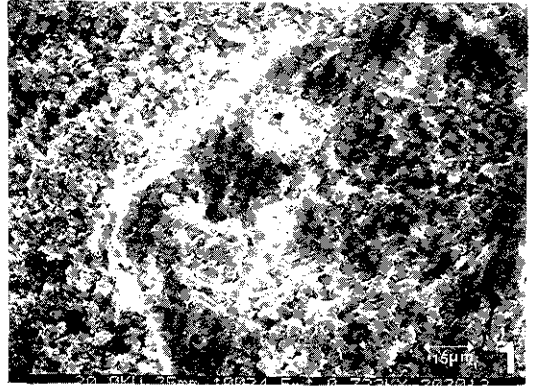


Fig. 13. SEM micrograph of Sulfated Fredonia Limestone. (Position 1 in Fig. 11.)

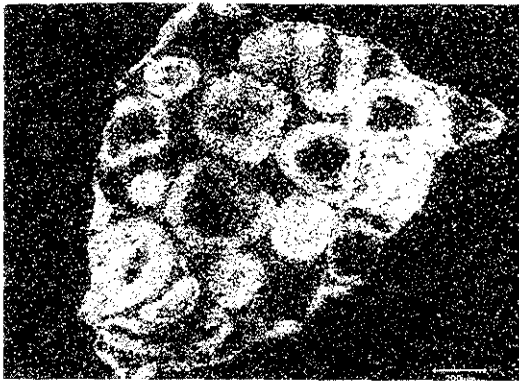


Fig. 12. SEM micrograph of Sulfated Fredonia Limestone. (S Distribution Map.)

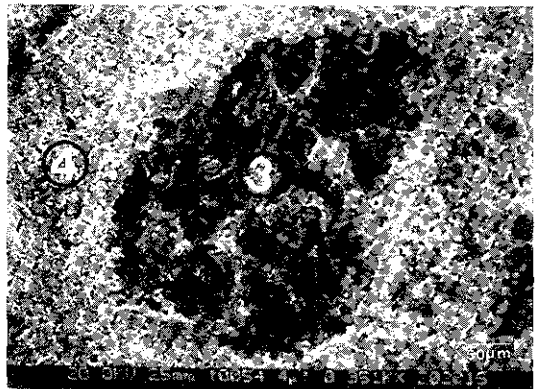


Fig. 14. SEM micrograph of Sulfated Fredonia Limestone. (Position 3 & 4 in Fig. 11.)

indications of pathways and of reasons for such S penetration. For example, Fig. 13 and 14 represents highly-porous structure with finely-divide crystallites of approximate dimensions 0.7~3 microns. Some of these finely-divided crystalline areas result from an oolitic origin while others result from fossil remnants. Central positions within the fossil remnants are generally not sulfated; these positions, labeled 2b and 3b in Fig. 11, consist of a semi-porous structure, with some crystallites, but mostly of a semi-terminating, amorphous layering structure. The areas labeled as 6b in Fig. 11 are

magnified in Fig. 15 which were non-porous and contained large grains of approximate dimensions of 40~150 microns. The S does not appreciably penetrate into these grains but does diffuse along the grain boundaries as in Fig. 16. Hence, the pathway of S into highly-porous areas within the particle is either by diffusion along grain boundaries or simply by diffusion from a highly-porous region to another porous region.

Not all particles of Fredonia limestone contain oolites and fossil remnant structure of  $\text{CaCO}_3$ . This fact is observed in the SEM



Fig. 15. SEM micrograph of Sulfated Fredonia Limestone. (Position 6 in Fig. 11.)

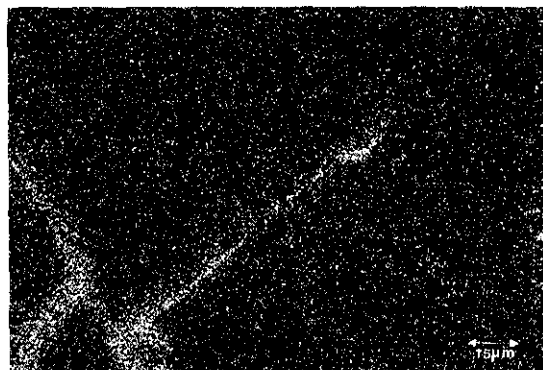


Fig. 16. SEM micrograph of Sulfated Fredonia Limestone Distribution Map from a Position Near 6 in Fig. 11.

micrograph and Ca and S elemental maps of several cross-sectioned, sulfated particles. The S map shows that S has penetrated into the interior as well as being concentrated in a near-surface shell<sup>9)</sup>. The S penetration into the interior cause relatively large cracks within the particle which may be originated within boundary regions between different crystallites of  $\text{CaCO}_3$ .

The SEM micrographs of cross-sectioned limestone particles after simultaneous calcination/sulfation are also examined. The distribution of S within the particles is similar to the

S distribution that was observed in sequentially-treated limestone. Penetration of S into the interior of the particles depends on whether the particles contain fossil remnant of oolitic structure. Particles that do not have such heterogeneity contain S primarily on their external surface in the form of a shell, in addition to some S which has penetrated into the particle via cracks or fissures that exist in the particle.

#### 4. CONCLUSION

Raw Fredonia limestone and sequentially and simultaneously calcined/sulfated limestones were examined by Hg porosimeter as well as SEM techniques to provide microstructural and compositional information. Hg porosimeter measurement of calcined limestone illustrated that surface area and pore volume are increased with decreasing particle size. The SEM studies of cross-sectioned particles showed that the surface of the calcined limestone particles to be more diffusive nature than the parent calcite. But the sulfur distribution pattern of simultaneously-treated particles and that of the sequentially-treated one has no difference.

#### ACKNOWLEDGEMENTS

Financial support for this research were provided by the Commonwealth of Kentucky and the Tennessee Valley Authority(TVA). The authors express thanks to James Byrd of TVA and John Stencil of Center for Applied Energy Research(CAER) in facilitating progress on this research. This work was performed at the CAER and was written at Korea.

#### REFERENCES

1. R. Harvey and J. Stenmetz : "Petrographic Properties of Carbonate Rocks Related to Their Sorption of  $\text{SO}_2$ ", Ill. State Geol.

- Survey, Environmental Geol. Notes, No. 50, NTIS, (1972) 37
2. J. Szekeley and J. Evans : Chem. Eng. Sci. 26 (1971) 1901
  3. C. Georgakis, C. Chang, and J. Szekeley : Chem. Eng. Sci. 34 (1972) 1072
  4. M. Hartman and R. Coughlin : AIChE J. 22 (1976) 490
  5. J. Stencel, H. T. Kim, and J. Heink : "Determination of Limestone Sulfation/Calcination Microstructural Behavior in the AFBC Environment", 2nd Quarterly Progress Report, Contract No. TV-64342A (1985)
  6. J. Stencel and H. T. Kim : "Determination of Limestone Sulfation/Calcination Microstructural Behavior in the AFBC Environment", Final Report, Contract No. TV-64342A (1986)
  7. R. Boynton : Chemistry and Technology of Lime and Limestone, 2nd ed., John Wiley & Sons, Inc., (1980) 43
  8. G. Freeman : Scanning Electron Microscopy 3 (1984) 1147